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Understanding the environmental impacts of large fissure eruptions: Aerosol and gas emissions from the 2014–2015 Holuhraun eruption (Iceland)



Evgenia Ilyinskaya^{a,*}, Anja Schmidt^a, Tamsin A. Mather^b, Francis D. Pope^c, Claire Witham^d, Peter Baxter^e, Thorsteinn Jóhannsson^f, Melissa Pfeffer^g, Sara Barsotti^g, Ajit Singh^c, Paul Sanderson^c, Baldur Bergsson^g, Brendan McCormick Kilbride^h, Amy Donovanⁱ, Nial Peters^j, Clive Oppenheimer^j, Marie Edmondsⁱ

^a School of Earth and Environment, University of Leeds, LS2 9JT, Leeds, UK

^b Department of Earth Sciences, South Parks Road, Oxford, OX1 3AN, UK

^c School of Geography, Earth and Environmental Sciences, University of Birmingham, Birmingham, B15 2TT, UK

^d Met Office, Fitroy Road, Exeter, Devon, EX1 3PB, UK

^e Cambridge Institute of Public Health, University of Cambridge School of Clinical Medicine, Cambridge, CB2 0SR, UK

^f Environment Agency of Iceland, Suðurlandsbraut 24, 108 Reykjavík, Iceland

^g Icelandic Meteorological Office, Bustaðavegi 7–9, 150 Reykjavík, Iceland

^h Department of Earth Sciences, University of Cambridge, Downing Street, Cambridge, CB2 3EQ, UK

ⁱ Department of Geography, King's College London, Strand Campus, WC2R 2LS, UK

^j Department of Geography, University of Cambridge, Downing Place, Cambridge, CB2 3EN, UK

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ABSTRACT

The 2014–2015 Holuhraun eruption in Iceland, emitted ~11 Tg of SO₂ into the troposphere over 6 months, and caused one of the most intense and widespread volcanogenic air pollution events in centuries. This study provides a number of source terms for characterisation of plumes in large fissure eruptions, in Iceland and elsewhere. We characterised the chemistry of aerosol particle matter (PM) and gas in the Holuhraun plume, and its evolution as the plume dispersed, both via measurements and modelling. The plume was sampled at the eruptive vent, and in two populated areas in Iceland. The plume caused repeated air pollution events, exceeding hourly air quality standards (350 µg/m³) for SO₂ on 88 occasions in Reykjavík town (100 km distance), and 34 occasions in Reykjavík capital area (250 km distance). Average daily concentration of volcanogenic PM sulphate exceeded 5 µg/m³ on 30 days in Reykjavík capital area, which is the maximum concentration measured during non-eruptive background interval. There are currently no established air quality standards for sulphate. Combining the results from direct sampling and dispersion modelling, we identified two types of plume impacting the downwind populated areas. The first type was characterised by high concentrations of both SO₂ and S-bearing PM, with a high S_{gas}/S_{PM} mass ratio (SO_{2(g)}/SO_{4²⁻}(PM) > 10). The second type had a low S_{gas}/S_{PM} ratio (<10). We suggest that this second type was a mature plume where sulphur had undergone significant gas-to-aerosol conversion in the atmosphere. Both types of plume were rich in fine aerosol (predominantly PM₁ and PM_{2.5}), sulphate (on average ~90% of the PM mass) and various trace species, including heavy metals. The fine size of the volcanic PM mass (75–80% in PM_{2.5}), and the high environmental lability of its chemical components have potential adverse implications for environmental and health impacts. However, only the dispersion of volcanic SO₂ was forecast in public warnings and operationally monitored during the eruption. We make a recommendation that sulphur gas-to-aerosol conversion processes, and a sufficiently large model domain to contain the transport of a tropospheric plume on the timescale of days be utilized for public health and environmental impact forecasting in future eruptions in Iceland and elsewhere in the world.

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* Corresponding author.

E-mail address: e.ilyinskaya@leeds.ac.uk (E. Ilyinskaya).

1. Introduction

Large fissure eruptions (>1 km³) are one of the most environmentally hazardous volcanic scenarios due to their prodigious

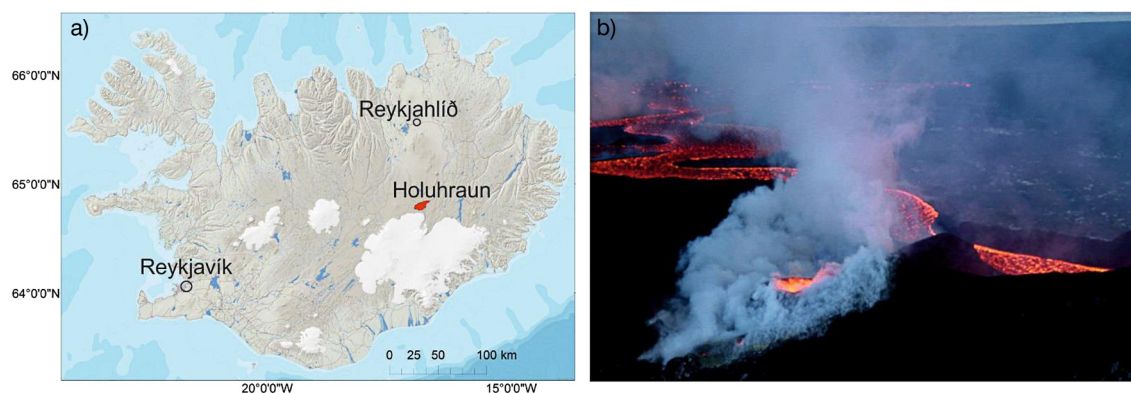


Fig. 1. **a)** Location map of the Holuhraun eruption site (lava flow extent shown by red colour), and the two populated areas in this study: Reykjavík city capital area, population 120,000; and Reykjavíhlíð town, population 300. **b)** Holuhraun eruption during the January 2015 field campaign. During this period the activity was exclusively effusive. The width of the lava flow is ~ 50 m. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

release of gases and aerosol into the troposphere and lower stratosphere. This can impact air quality, terrestrial and aquatic environments, climate and health (Robock, 2000; Schmidt et al., 2011; Thordarson and Self, 2003; Witham et al., 2015). Icelandic large fissure eruptions were included in the UK National Risk Register in 2012 as one of the highest priority risks, due to the significant societal consequences caused by the Laki eruption 1783–1784 CE (15 km^3 lava, estimated 120 Tg SO_2 , Thordarson and Self, 2003) across the northern hemisphere. During the Laki eruption, a thick sulphate aerosol veil and fluoride contamination of pasture and drinking water for livestock, led to the loss of $\sim 20\%$ of Iceland's population through famine (Thordarson and Self, 2003). It has been suggested that mortality in the UK and mainland Europe also increased (Schmidt et al., 2011; Witham and Oppenheimer, 2004). Large fissure eruptions are often assumed to be the closest analogues for large igneous province volcanism during the human era (e.g., Self et al., 2014) and so understanding them is further important in order to gain deeper insights into these massive environmental perturbations that punctuate Earth history. The Holuhraun eruption in Iceland in 2014–2015 (Fig. 1) is the largest such event since Laki and presents us with a rare opportunity to study volcanism of this style and scale using modern scientific techniques.

Tropospheric plumes from eruptions with low-level explosivity are complex mixtures of magmatic gases, entrained background air and aerosol particulate matter (PM), and usually low quantities of silicate ash. Volcanic plumes are known to contain nearly all naturally occurring elements (e.g., Allard et al., 2000; Symonds et al., 1992) ranging from the common metals (Na, K, Ca, Mg) to trace species (e.g., Pb, Mo, As, Se, Hg and Br). The interactions of this range of elements with ecosystems are highly variable and deposition of plumes can be either adverse or beneficial for terrestrial and aquatic environments (e.g. Cronin and Sharp, 2002; Jones and Gislason, 2008).

Volcanic gases and PM may also present a health hazard through air pollution. Sulphur dioxide (SO_2) levels in particular often exceed official air quality standards for this gas in the ambient air (Gislason et al., 2015; Schmidt et al., 2015; Tam et al., 2016). A large proportion of volcanic PM is in the $\text{PM}_{2.5}$ fraction (sub- $2.5 \mu\text{m}$ diameter), which has become a key metric in air pollution guidelines. Short and long term exposure to $\text{PM}_{2.5}$ in the ambient air is estimated to cause over 3 million premature deaths globally per year (Lim et al., 2012), and it remains the single largest environmental health risk in Europe (Holgate, 2017). Detailed information on SO_2 and PM size-resolved mass flux, and gas and PM composition, is therefore necessary for reliable assessments of the effect of volcanic emissions on the environment and health.

The Holuhraun eruption occurred in the central highlands of Iceland (Fig. 1), on the ice-free part of Bárðarbunga volcanic system and lasted 6 months from 31 August 2014 to 28 February 2015. The estimates of its total SO_2 emission range between 11 Tg (Gislason et al., 2015) and 19 Tg (Gauthier et al., 2016), 1.5–2 times more than the total anthropogenic SO_2 emissions from the European Economic Area in 2011 (European Environmental Agency, 2017). Daily SO_2 gas fluxes averaged 60 kt/day (Gislason et al., 2015), a rate of outgassing rarely observed during sustained eruptions. It dwarfed most other long-term volcanic SO_2 emitters, such as Kilauea volcano in Hawaii (2–8 kt/d, Elias and Sutton, 2012) and Mt Etna, Italy (3.5 kt/d between 2005 and 2008, Salerno et al., 2009). It was one of the largest global tropospheric volcanic emissions since Laki, rivalled only by emission from Miyakejima 2000–2003 ($\sim 18 \text{ Mt SO}_2$, Kazahaya et al., 2004). This caused frequent and persistent deterioration of air quality in Iceland with regard to SO_2 (Gislason et al., 2015), and an impact on the chemistry of snow and rain precipitation around Iceland (Galeczka et al., 2016; Gislason et al., 2015; Stefánsson et al., 2017). Long-range periodic impacts on air quality were reported in the UK, Ireland, Finland, the Netherlands and Austria (Gislason et al., 2015; Schmidt et al., 2015; Twigg et al., 2016).

Our study quantifies the impact of Holuhraun on populated areas in Iceland. Specifically we trace the evolution of the plume chemistry from the eruption site to 2 key areas of population: Reykjavíhlíð, which is the nearest municipality to Holuhraun at 100 km distance, and Reykjavík capital area, which hosts $\sim 60\%$ of Iceland's population, 250 km distance (Fig. 1). We present a novel dataset of gas and size-resolved aerosol chemistry, including a time series of constituents relevant for air quality assessment, i.e., SO_2 , $\text{PM}_{2.5}$ and sulphate aerosol, and analysis of trace species including heavy metals. The findings of this study are relevant for multiple other countries impacted by volcanic emissions, either through prolonged eruptions, for example that of Kilauea in Hawaii, or through persistent quiescent degassing, such as from Masaya in Nicaragua.

2. Methodology

Data were collected at 3 sites (Fig. 1, section 2.1). The instrumentation and analytical techniques are detailed in sections 2.2–2.6.

2.1. Site descriptions

2.1.1. Holuhraun eruption site

The field campaign took place 21–22 January 2015, when we had favourable winter weather, dry and generally bright, thick

Table 1
Sampling sites, dates and instruments.

Location	Date	Instrument	Sample (S) or optical (O)	Sample ID	Distance (km) & direction from main vent	Sampling duration (hh:min)	Total volume (m ³)
Eruption site, airborne plume	21/01/2015	FP	Bulk aerosol and gas (S)	Loc2_FP	< 4, N	00:15	0.01
Eruption site, grounding plume	21/01/2015	FP	Bulk aerosol and gas (S)	Loc1_FP	5, N	03:15	2.3
				Loc6_FP	20, N	03:00	2.2
Eruption site, grounding plume	21/02/2015	FP	Bulk aerosol and gas (S)	Loc6b_FP	20, N	08:00	5.8
				Loc12_FP	5, N	06:03	4.4
				Loc13_FP	5, N	05:20	2.6
				Loc13_M	5, N	05:20	1.6
		Moudi-13	Size-resolved aerosol (S)				
Reykjahlíð town	01/01/2014–28/02/2015	AQ	Gas phase SO ₂ (O)	Reykjahlíð SO ₂	100, N	n/a	n/a
	20–24/01/2015	Moudi-8	Size-resolved aerosol (S)	DW_M	100, N	90:00	130
	21–24/01/2015	OPC	Size-resolved aerosol (O)	DW_OPC	100, N	68:50	5
	20–21/01/2015	FP	Bulk aerosol and gas (S)	DW_20/21	100, N	12:00	8.6
	21–22/01/2015			DW_21/22	100, N	12:00	8.6
	22–23/01/2015			DW_22/23	100, N	12:00	8.6
	23–24/01/2015			DW_23/24	100, N	12:00	8.6
Reykjavík capital area	02/01/2012–28/01/2015	AQ	Gas phase SO ₂ (O)	RVK_SO ₂	250, SW	n/a	n/a
		AQ	PM10 and PM _{2.5} (O)	RVK_PM	250, SW	n/a	n/a
	02/01/2014–28/01/2015	AQ	Bulk aerosol (S)	RVK_SO ₄	250, SW	n/a	n/a

FP – filter pack for bulk aerosol and gas sampling (section 2.2); SKC – 5 stage aerosol impactor; Moudi-13 – 13-stage impactor; Moudi-8 – 8-stage impactor (2.3); OPC – GRIMM optical particle counter (2.4); AQ – air quality station (2.5 and 2.6).

snow cover on the ground and -10°C . The eruptive activity was exclusively effusive at the time, with lava issuing from the main vent Baugur and flowing towards N–NE (Fig. 1b). Due to the low wind speed (≤ 5 m/s) and high thermal flux of the eruption the plume grounded only periodically. We collected direct samples of the plume using filter packs (section 2.2) and cascade impactors (section 2.3), both on the ground in a dilute plume and in the highly concentrated airborne plume with the assistance of an Iceland coast guard helicopter (Table 1). We collected a repeat sample from a helicopter two months after the eruption finished to eliminate the possibility that the helicopter could be a source of detectable contamination.

2.1.2. Reykjavík town (100 km downwind)

Reykjavík is a rural town with ~ 300 inhabitants, located inland in north Iceland. It is the closest municipality to Holuhraun. Continuous automated monitoring of SO₂ gas concentrations was operated by the Environment Agency of Iceland (EAI) both before and during the eruption (section 2.5). We obtained additional measurements during a field campaign 20–24 January 2015. Reykjavík was selected as the downwind location for the field campaign based on the plume-dispersion forecast issued by the Icelandic Meteorological Office (IMO). The plume was present at this location for most of the field campaign, as shown by the forecast and later supported by our data. Direct sampling of gas and aerosol (sections 2.2 and 2.3) and an optical particle counter (sections 2.4) were set up outside a local school, within ~ 100 m from the automated SO₂ monitoring station.

2.1.3. Reykjavík capital area (250 km downwind)

Reykjavík capital area is located in south-west Iceland and has $\sim 200,000$ inhabitants, which is 60% of Iceland's total population. It is a coastal city where non-volcanic air pollution is sourced mostly from anthropogenic activities (including one aluminium smelter) and sea-spray. Continuous automated monitoring of SO₂ and PM_{2.5} was done both before and during the eruption at Hvaleyrarholt EAI station (section 2.5). Sulphate was analysed on filter samples collected daily at the same station (section 2.6).

2.2. Filter packs

Filter packs were used to collect simultaneous samples of gas and PM. We followed the technique described by (Allen et al., 2000). The filter packs comprised one PM filter followed by 2–4 base-treated gas filters in an all-Teflon three-stage cartridge. The PM filter (Millipore, 47 mm, AAWP, pore size $0.8\ \mu\text{m}$) collects all particle size bins in bulk. The filters for gas sampling were Whatman 41 mm ashless circles impregnated with 5% K₂CO₃ and 1% glycerol in distilled deionized (DI) water, following the preparation technique described in Martin et al. (2010) and Pfeffer et al. (2013). This base treatment captures acidic gases (e.g., SO₂, HF and HCl) on the filters. Blank filters were transported into the field and transferred to the sample bags in the same way as the sampling filters. This ensured that there was no unaccounted contamination due to transport and handling of the filters in the field. Airflow through the filter pack was generated using external pumps. After sampling, the filter pack was closed by a plastic lid to prevent particle loss and contamination. Once indoors, filters were then transferred into individual polypropylene bags (2 layers).

A three-stage sequential leaching scheme was employed to assess the solubility of metals in the PM, following the procedure used in Mather et al. (2012). In summary: (i) The first stage extracted the environmentally labile fraction by using ultraclean water for the leaching. (ii) The second stage leached moderately environmentally-labile material by adding a weak acid, hydroxylamine hydrochloride in 25% acetic acid to the residues from step 1. (iii) The third stage extracted the environmental immobile fraction of the PM (bound to silicates) by using HF. Following extraction, all samples were analysed for metals using an ICP-MS. Anions (Cl[−], F[−] and SO₄^{2−}) were analysed in the extracts from the first extraction stage only (water-soluble fraction) using ion chromatography (IC). The base-treated gas filters were analysed using IC only. All analysis was performed at the British Geological Survey laboratories in Keyworth, UK.

2.3. Aerosol cascade impactors

Cascade impactors allow size-segregated sampling of PM and have been used in multiple studies of volcanic aerosol (e.g., Ilyinskaya et al., 2012, 2010; Martin et al., 2011, 2010). A cascade

impactor consists of a series of stages with nozzles of decreasing diameter. An external pump attached to the impactor outlet creates an airflow through the stages. Beneath each stage is an impaction plate (where a filter is mounted) upon which the air jet impinges and where a fraction of the suspended aerosol particles is collected. Larger particles are deposited at the early separation stages whereas fine particles are not deposited until they have passed through correspondingly narrower nozzles in which the gas flows at higher velocities (e.g., Marple et al., 1991). The cut-off particle diameter for each impactor stage is conventionally reported as D_{50} which is the diameter of particles retained with 50% efficiency on each stage.

Here we used two types of cascade impactors (Table 1):

1) Micro Orifice Uniform Deposition Impactor (nano-MOUDI, model 125NR, MSP corporation), operating at 10 l/min. It resolves 13 size bins between 18 and 0.01 μm cut-off diameter. PM larger than 18 μm is collected on the inlet stage, and PM < 0.01 μm on the after-stage. Filters used were PTFE, 47 mm, 0.2 μm pore size. The last impaction stage (0.018–0.01 μm) was missing and not used during this campaign. This does not affect the PM cut-off sizes on the preceding stages.

2) MOUDI (model 130, MPS corporation), operating at 30 l/min. It resolves 8 size bins between 18 and 0.18 μm cut-off diameter. PM larger than 18 μm is collected on the inlet stage, and PM < 0.18 μm on the after-stage. PTFE filters of 47 mm diameter and 1.0 μm pore size (Whatman 7590-004) were used for the main stages and a similar 37 mm filter (Whatman 7590-003) on the after-stage.

The filters (including procedural blanks) were handled and analysed using the same procedures as in section 2.2.

2.4. Optical particle counter

A GRIMM optical particle counter (model 1.107) was used in Reykjavík. The GRIMM data provides size segregated data for PM mass concentration and 8 particle size bins are resolved in the range 0.5 to >15 μm . Particle diameter data are automatically converted to particle volume using mean particle diameter between the thresholds of the 31 different channels, assuming spherical particles. Volume data are converted to a mass distribution using an instrument-specific density factor of 2.8 using standard protocols developed by GRIMM (Grimm and Eatough, 2009). Factory settings were used in this analysis.

2.5. Continuous SO_2 and PM monitoring

Gaseous SO_2 concentration is routinely monitored around Iceland by the EAI air quality stations. Automated SO_2 stations both in Reykjavík and Reykjavík were in operation before the onset of the eruption. The SO_2 measurements are done by an analyser equipped with a pulsed fluorescence spectroscopy meter, recording 10- and 60-min average concentration. All of the analysers are calibrated at 6-month intervals. The detection limit is 2 $\mu\text{g m}^{-3}$ and the uncertainty is 5%.

PM_{10} and $\text{PM}_{2.5}$ is automatically monitored at 14 stations in Iceland. Five of these are in the Reykjavík capital area. There is no permanent automated monitoring of PM at Reykjavík.

For Reykjavík, we analysed SO_2 , PM_{10} and $\text{PM}_{2.5}$ data from Hvaleyrarholt station, which is also the only station to monitor sulphate through direct sampling (section 2.6). Non-volcanic background values of SO_2 , PM_{10} and $\text{PM}_{2.5}$ were calculated based on the period from 2 January 2012 to 30 August 2014, an interval with no volcanic eruptions. New Year's Eve (29 December to 1 January each year) was excluded from all calculations due to noticeable firework/bonfire pollution with $\text{PM}_{2.5}$ reaching a maximum of 140 $\mu\text{g m}^{-3}$ in 2012.

For Reykjavík, we analysed SO_2 data from the automated station. Non-volcanic SO_2 background was calculated based on the period from 2 January 2014 to 30 August 2014. Non-volcanic PM_{10} background was calculated from daily filter samples (24 h-average) collected in the same municipality between 2000 and 2005 (EAI data). We used only samples collected in the month of January as the PM mass concentrations fluctuate during the year, with highest concentrations during the summer months (May–August PM_{10} $7.3 \pm 9.3 \mu\text{g m}^{-3}$) and lowest during winter time (November–February PM_{10} $4.1 \pm 3.7 \mu\text{g m}^{-3}$) when snow cover minimizes re-suspension of rock dust, and agricultural and other anthropogenic activities (e.g. tourism traffic) are reduced. 1 January was excluded from the background concentrations due to New Year's Eve pollution of up to 25 $\mu\text{g m}^{-3}$ PM_{10} . Background $\text{PM}_{2.5}$ is not known but is assumed to be lower than Reykjavík ($4.1 \mu\text{g m}^{-3}$) as this is a rural inland area.

2.6. Sulphate monitoring (Reykjavík only)

Aerosol samples were collected using Digital DHA-80 filter sampler located at Hvaleyrarholt station. The filters used (fibre glass and quartz) were not treated to collect gaseous phases. The filters were changed once every 24 h. After sampling, the filters were washed with DI water and peroxide solution and analysed for sulphate ion concentration using ion chromatography. The sample extraction and analysis were done at the Innovation Centre of Iceland. Non-volcanic sulphate background was calculated based on the period from 2 January 2014 to 30 August 2014.

3. Results

The chemical composition of the bulk plume (gas and aerosol phases) at the three sampling sites is summarised in Fig. 2. Full analytical results are in the supplementary material (Table SM and Fig. SM1).

3.1. Plume gas phase

The maximum gas concentrations were detected in the near-vent airborne plume, with 15-min average value of 43,000 $\mu\text{g m}^{-3}$ SO_2 , 530 $\mu\text{g m}^{-3}$ HCl and 210 $\mu\text{g m}^{-3}$ HF. The average concentrations in the grounding plume 4–20 km from the vent were 3,100 \pm 2,900 $\mu\text{g m}^{-3}$ SO_2 , 19 \pm 2.3 $\mu\text{g m}^{-3}$ HCl and 11 \pm 9.5 $\mu\text{g m}^{-3}$ HF.

In Reykjavík (100 km downwind) the hourly-mean and maximum concentrations of SO_2 gas (26 \pm 120 $\mu\text{g m}^{-3}$, and 1700 $\mu\text{g m}^{-3}$, respectively) during the eruption significantly exceed the pre-eruption background levels (0.41 \pm 0.24 $\mu\text{g m}^{-3}$, and 2.4 $\mu\text{g m}^{-3}$, respectively), Fig. 3 and Table 2. During 20–24 January 2015, the gas composition in the grounding plume was 370 \pm 710 $\mu\text{g m}^{-3}$ SO_2 , 4.5 \pm 4.8 $\mu\text{g m}^{-3}$ HCl and 1.5 \pm 1.8 $\mu\text{g m}^{-3}$ HF.

Reykjavík data (Fig. 3, 250 km downwind) were analysed as a function of the prevalent wind direction, as there is a noticeable direction-dependent difference in the background concentrations of gas and PM (Table 2). Background SO_2 was higher during westerly winds compared to easterly winds (1.8 \pm 1.4 vs 1.2 \pm 0.8 $\mu\text{g m}^{-3}$, respectively). The most likely sources of these pollutants from the west of the sampling location are the open sea (sea-spray) and an aluminium smelter. However, during the eruption, the increase in average SO_2 is greater for the intervals of easterly winds than westerly winds, as the eruption site was located to the east of Reykjavík. The average and maximum concentrations of SO_2 during the eruption (3.2 \pm 0.8 and 15 $\mu\text{g m}^{-3}$, respectively) significantly exceed the background levels. We considered the plume to be present in Reykjavík when total sulphur in the atmosphere ($S_{\text{total}} = S_{\text{gas}} + S_{\text{PM}}$) during a 24 h interval exceeded the maximum S_{total} measured before the eruption onset

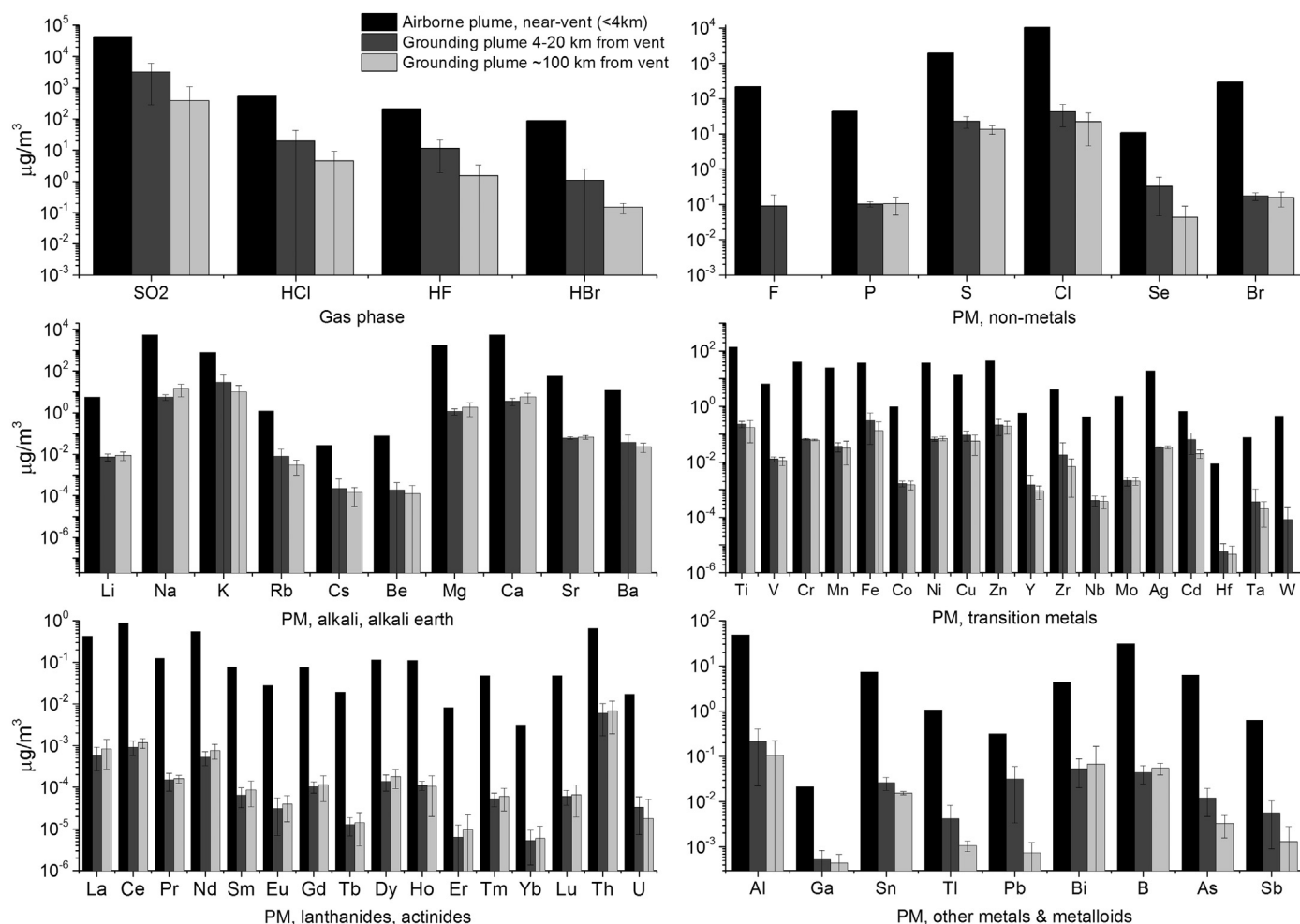


Fig. 2. Chemical composition of the plume gas phase and PM at three representative sampling locations: (i) airborne young and concentrated plume <4 km from emission source (1 sample); (ii) grounding plume at the eruption site, 4–20 km from emission source (5 samples); (iii) grounding plume in a populated area (Reykjahlíð) 100 km from emission source (4 samples). All samples were collected on 21 January 2015. The y-axis is on a log scale.

(30 $\mu\text{g}/\text{m}^3$). Based on this analysis the volcanic plume was present in Reykjavík for 38 out of the 181 days of eruption. On those days, the average SO_2 concentrations were $72 \pm 140 \mu\text{g}/\text{m}^3$ (Table 2).

3.2. Plume aerosol phase

The near-vent airborne plume had extremely high mass concentrations of PM, with a 15 min average of $25,000 \mu\text{g}/\text{m}^3$. The sample collected in the near-vent airborne plume was not size-resolved, but the size-resolved plume sample collected in the near-vent grounding plume showed that $\text{PM}_{2.5}$ accounted for 75–83% of the total PM. $\text{PM}_{2.5}$ mass in the grounding plume at the eruption site was $60 \mu\text{g}/\text{m}^3$ (1 sample, concentration averaged 5 h).

The grounding downwind plume in Reykjavík town had an average $\text{PM}_{2.5}$ concentration of $13 \pm 9.5 \mu\text{g}/\text{m}^3$ (70-h average value, Fig. 3). In Reykjavík capital area, the average daily $\text{PM}_{2.5}$ concentration throughout the whole eruption was $5.0 \pm 4.2 \mu\text{g}/\text{m}^3$, compared to 4.1 ± 3.6 before the eruption (Fig. 3). There was no significant difference between the daily and hourly averages of $\text{PM}_{2.5}$ concentration. The effect of the wind direction on the concentration of $\text{PM}_{2.5}$ was much less significant than on SO_2 (Table 2). The average sulphate concentration in Reykjavík during the eruption was twice as high as the pre-eruptive levels (3.0 ± 2.9 and $1.5 \pm 1.1 \mu\text{g}/\text{m}^3$, respectively), with some wind field-dependent variations. During the 38 days when the plume was present in Reykjavík, SO_4^{2-} accounted for 90% of the $\text{PM}_{2.5}$ mass on average, with the average SO_4^{2-} concentration of $6.3 \pm 3.7 \mu\text{g}/\text{m}^3$ (Table 2).

When interpreting the composition of highly dilute plumes sampled at more than a few km from source, such as at Reykjavík town, we have to account for a degree of mixing between the volcanic emissions and background air. In order to assess the extent of background air dilution of the Holuhraun plume at different sampling locations, we compare the sulphur to chlorine (S/Cl) molar ratio in volcanic PM with that of non-volcanic background PM, see supplementary material Fig. SM2. The PM collected near the emission source is concluded to have a predominantly volcanic chemical signature based on its S/Cl molar ratio (0.1–200, vs 0.05 in the background). The PM sampled in a more dilute plume 100 km downwind (Reykjavík) shows a higher degree of mixing with background PM (S/Cl 0.06–0.85), as is expected.

Different size fractions of the sampled PM appear to have different sources, volcanic and non-volcanic. The near-vent PM is of volcanic origin in all of the resolved size fractions (0.1 to $>18 \mu\text{m}$ diameter), as shown by source appointment analysis described in Fig. SM2. The sample collected 100 km from eruption site (in Reykjavík) shows that $\text{PM} < 1.8 \mu\text{m}$ has a predominantly volcanic composition, while $\text{PM} 1.8\text{--}5.6 \mu\text{m}$ is mostly non-volcanic, although some degree of plume contribution cannot be excluded. $\text{PM} \geq 10 \mu\text{m}$ diameter shows a high degree of mixing between the two sources. This suggests that there is important surface controlled growth of the SO_4^{2-} particles at relatively low supersaturation during long-range ($\geq 100 \text{ km}$) transport (Fig. SM2). Fig. 4 summarises the size-resolved chemistry of the aerosol phase, and its attributed

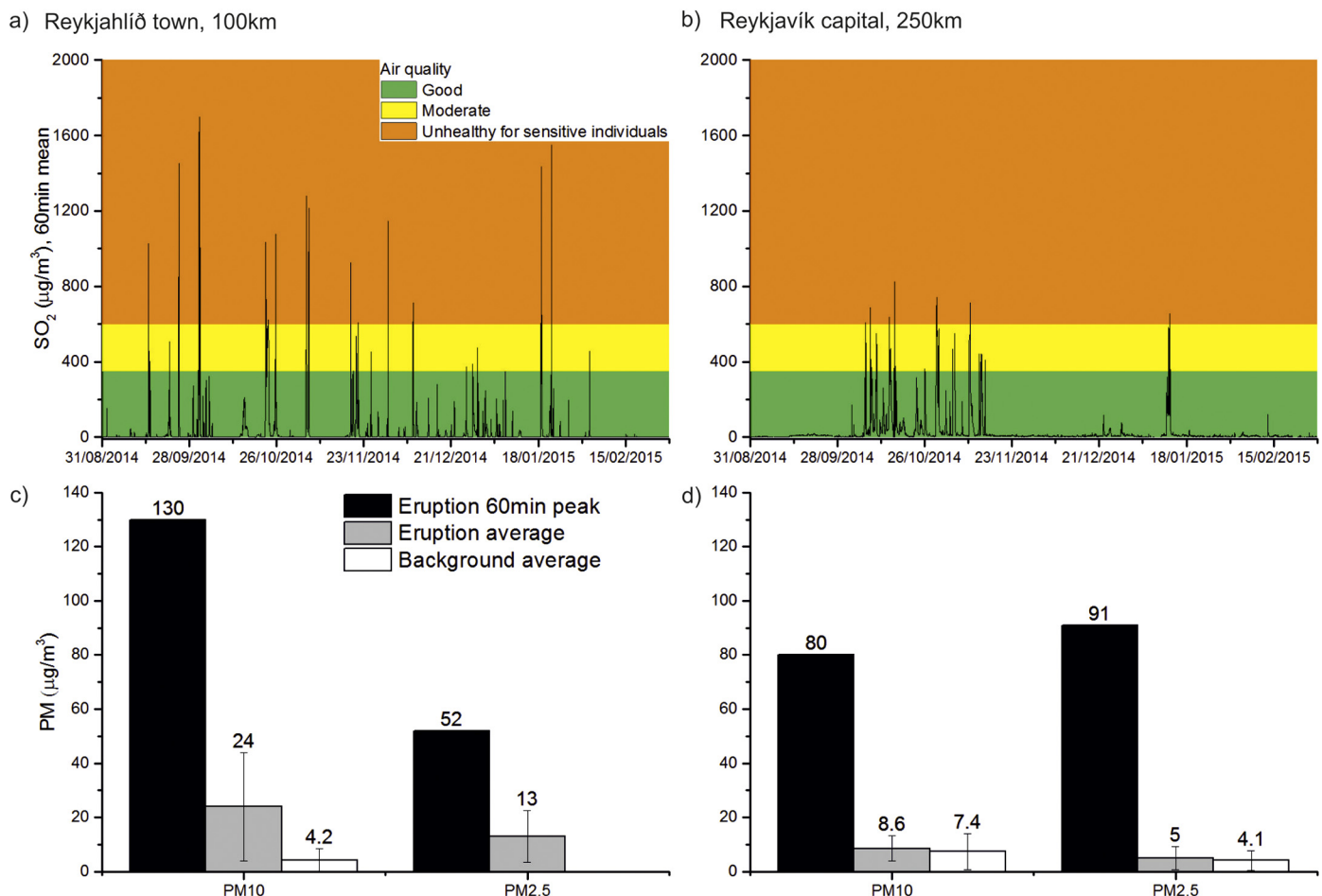


Fig. 3. Impact of the Holuhraun eruption on air quality in two populated areas. Top panel: time series of SO_2 concentrations in **a)** Reykjavík, and **b)** Reykjavík. Air quality guidelines from WHO/EU. Bottom panel: Aerosol concentrations in PM_{10} and $\text{PM}_{2.5}$ size fractions in **c)** Reykjavík, and **d)** Reykjavík.

source in samples from the eruption site and in Reykjavík. It shows that most of the analysed chemical species in the volcanic aerosol are in the $\text{PM}_{2.5}$ and PM_{10} size fractions.

4. Discussion

4.1. Plume composition

The gas phase mass ratios measured at the eruption site, HCl/SO_2 (0.026 ± 0.05) and HF/SO_2 (0.013 ± 0.02), are in good agreement with values (0.024 ± 0.07 and 0.011 ± 0.03 , respectively) measured by Stefánsson et al. (2017), who also sampled the near-vent plume using filter packs. The standard deviation of gas concentrations between individual samples was generally high (Fig. 2), showing that the grounding plume varied significantly in its gas phase concentration over short time scales. It is possible that the sampled gas was sourced partially from the degassing lava flows which generally has higher halogen/sulphur ratios (Thordarson et al., 1996), in addition to the gas from the main vent.

On average, the concentrations of the gas species decreased by ~ 1 – 2 orders of magnitude between the airborne plume and the grounding plume near the eruption site. The gas concentrations decreased by ~ 1 order of magnitude between sampling in the grounding plume near the eruption site and in Reykjavík at 100 km distance (Fig. 2).

By sampling the Holuhraun plume at varying distances from the eruptive vent we are able to show how sulphur in the volcanic plume fractionates between gas and aerosol phases over

time. The concentration of the volcanogenic plume components decreases with time due to more extensive mixing and dilution by background air as the plume ages. The decrease in total S concentration ($S_{\text{total}} = S_{\text{gas}} + S_{\text{PM}}$) in the plume and the ensuing change in $S_{\text{PM}}/S_{\text{gas}}$ ratio is used here as a proxy for an increasing plume age. Fig. 5 shows that $S_{\text{PM}}/S_{\text{gas}}$ ratio is markedly higher when the plume is more dilute (i.e. older), with a strong negative correlation of $\rho = -0.81$. This is consistent with sulphur undergoing gas-to-particle conversion in the Holuhraun plume, reaching a $S_{\text{PM}}/S_{\text{gas}}$ ratio of 0.62 in a sample taken at 100 km distance from the vent in Reykjavík 23–24 January 2015 (range of values 0.006–0.62), and up to 0.38 in Reykjavík at 250 km distance (range of values 0.016–0.38).

The relative abundance of sulphur and chlorine differs significantly between the gas and aerosol phases in the plume sampled shortly after its emission (Fig. 2). On average, the concentration of gaseous SO_2 exceeds HCl by a factor of 40. However, in the aerosol phase sulphur is less abundant than chlorine. It is known that $S_{\text{PM}}/\text{Cl}_{\text{PM}}$ is controlled not just by the magmatic gas composition but also by the atmospheric conditions. Our previous work (Ilyinskaya et al., 2012) showed that on emission chloride condenses into the aerosol phase much more readily when the ambient temperature is low ($< 0^\circ\text{C}$), while near-vent sulphate formation is unaffected, thereby lowering the $S_{\text{PM}}/\text{Cl}_{\text{PM}}$. This is applicable to the Holuhraun eruption as air temperatures were -5°C to -10°C at the time of sampling. Some mixing with background aerosol, which has a lower $S_{\text{PM}}/\text{Cl}_{\text{PM}}$ ratio (0.05, Bruland, 1983) compared to the volcanic aerosol (0.37 ± 0.30 , this study), is also occurring, as shown in the supplementary material (Fig. SM2).

Table 2

Impact of Holuhraun eruption on concentration of air pollutants (SO_2 , SO_4^{2-} and $\text{PM}_{2.5}$) in two populated areas. Reykjavík time series covers the whole eruption and is analysed here based on the prevalent wind direction, easterly ($0\text{--}179^\circ$), and westerly ($180\text{--}359^\circ$). 'Plume present' is identified when S_{total} ($S_{\text{gas}} + S_{\text{PM}}$) exceeded maximum background S_{total} . Reykjahlíð time series for $\text{PM}_{2.5}$ and SO_4^{2-} covers 21–24 January 2015, during which the plume was present. Exceedance of air quality standards is indicated where data covered the whole eruption. While no air quality standards exist for SO_4^{2-} we identified number of days exceeding daily-mean of $5 \mu\text{g}/\text{m}^3$. Background data for $\text{PM}_{2.5}$ and SO_4^{2-} does not exist for Reykjahlíð but they are considered to be lower than for Reykjavík due to its rural location. Units $\mu\text{g}/\text{m}^3$. 'b.d.l.' – below detection limits.

Reykjavík capital area, 250 km downwind										Reykjahlíð town, 100 km downwind							
		Background (SO_2 , $\text{PM}_{2.5}$ 02/01/2012–30/08/2014; SO_4^{2-} 01/01/2014–30/08/2015)				Eruption (31/08/2014–28/02/2015)				Background (02/01/2014–30/08/2015)				Eruption (SO_2 31/08/2014–28/02/2015; $\text{PM}_{2.5}$, SO_4^{2-} 21–24/01/2015)			
Conditions		Average	σ	Max	Min	Average	σ	Max	Min	Average	σ	Max	Min	Average	σ	Max	Min
SO_2 (hour-mean)	Easterly wind	0.8	1.4	38	b.d.l.	23	84	1400	b.d.l.	0.41	0.24	2.4	b.d.l.	26	120	1700	0.0
	Westerly wind	1.9	4.4	59	b.d.l.	8.8	23	260	b.d.l.								
	Plume present (38 days)	n/a	n/a	n/a	n/a	72	140	1400	b.d.l.								
	Air quality exceedance (1 h > $350 \mu\text{g}/\text{m}^3$ or 24 h > $125 \mu\text{g}/\text{m}^3$)	0 hours/days				34 hours/7 days				0 hours/days				88 hours/10 days			
$\text{PM}_{2.5}$ (hour-mean)	Easterly wind	4.1	5.2	160	b.d.l.	4.8	5.2	91	b.d.l.		n/a			13	9.5	52	1.1
	Westerly wind	4.0	5.1	160	b.d.l.	4.9	5.2	53	53								
	Plume present (38 days)	n/a	n/a	n/a	n/a	7.5	6.0	91	b.d.l.								
	Air quality exceedance 24 h > $25 \mu\text{g}/\text{m}^3$	4 (in 32 months)				0											
SO_4^{2-} (daily-mean)	Easterly wind	1.2	0.8	3.5	0.2	3.2	3.0	15	0.0		n/a			11	10	25	2.3
	Westerly wind	1.8	1.4	6.5	0.0	2.7	2.7	14	0.0								
	Plume present (38 days)	n/a	n/a	n/a	n/a	6.3	3.7	15	0.0								
	> $5 \mu\text{g}/\text{m}^3$	8 days (in 8 months)				39 days, thereof 30 of volcanic source (in 6 months)								n/a			

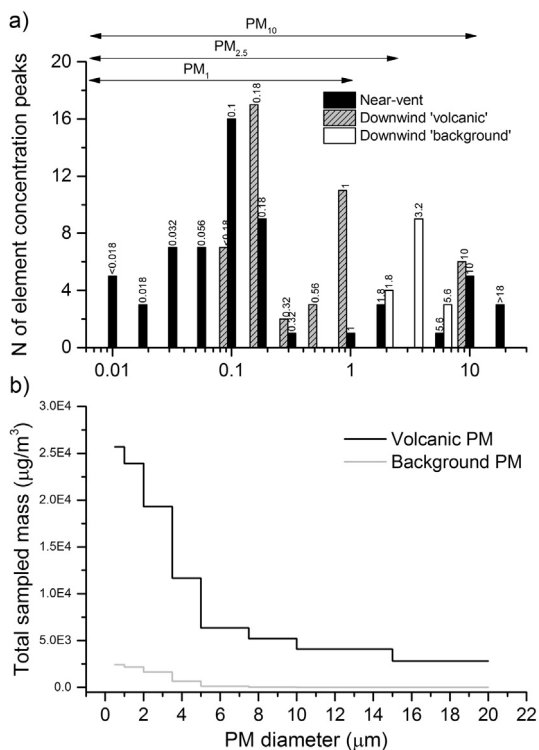


Fig. 4. **a)** Size-resolved distribution of chemical species (elements and ions) sampled in a near-vent plume (~ 5 km from source), and in a dilute downwind plume in Reykjavíð (~ 100 km from source). The downwind aerosol contains particles from two distinct sources, volcanic and background, with different sources dominating different size bins. The figure also shows definitions of aerosol sizes used in air pollution and health impact literature, PM_1 (diameter < 1.0 μm), $PM_{2.5}$ (< 2.5 μm) and PM_{10} (< 10 μm). **b)** Comparison of PM size distributions in the volcanic plume and non-volcanic background air, based on measurements in Reykjavíð. The y-axis shows the total mass in each size bin sampled during a continuous measurement 21–24 January 2015.

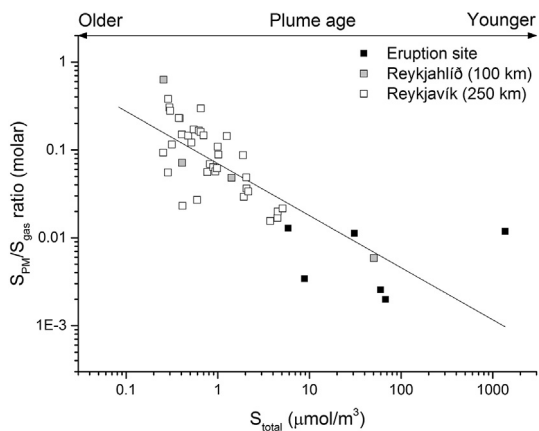


Fig. 5. Relationship between the plume concentration ($S_{total} = S_{gas} + S_{PM}$) and the S_{PM}/S_{gas} ratio. The plume concentration is a proxy for plume age. The data points are from the eruption site (6 samples), Reykjavíð (4 samples), and Reykjavík (35 samples from days when the plume was present, and had $S_{PM}/S_{gas} > 0$).

There are also differences in the size distribution of volcanic and background aerosol (Fig. 4b), as identified by the high time-resolution measurements from Reykjavíð 21–24 January 2015. The plume was interpreted to be present during time intervals where PM_{total} mass exceeded $10 \mu g/m^3$. This is justified for this relatively short sampling interval during the time of year when non-volcanic aerosol is very low in this inland part of Iceland (background aerosol data presented in section 2.5), although this may not hold true for coastal areas which receive increased aerosol of marine

origin during winter months (Gislason et al., 1996). Fig. 4 shows that the size distributions of PM mass concentration during plume presence is markedly different from the background. Within the plume the particles in the smallest aerosol size bins (~ 0.5 – $3.2 \mu m$ diameter) are greatly enhanced compared to background. Furthermore, a coarse mode ($> 7.5 \mu m$ diameter) is present in the plume and not in the background aerosol.

This shows that the finest and the coarsest PM size fractions (< 1.8 and $\geq 10 \mu m$ diameter) are predominantly volcanic. This is in good agreement with measurements of volcanic plumes from non-explosive activity elsewhere, in particular in locations characterised by sub-zero temperatures such as Erebus volcano in Antarctica (Ilyinskaya et al., 2010) and Fimmvörðuháls fissure eruption in Iceland (Ilyinskaya et al., 2012), where the dominant aerosol mode in a plume within a few minutes of emission is $\sim 0.2 \mu m$ in diameter. Plumes of similar age that are emitted into a warmer and more humid atmosphere have a dominant aerosol mode of ~ 0.5 – $1.0 \mu m$ diameter, e.g. at Masaya in Nicaragua (Martin et al., 2011), Kiluaea in Hawaii (Mather et al., 2012), and various volcanoes in Italy (Martin et al., 2008; Mather et al., 2004).

Exposure standards are not established for most trace chemicals in airborne aerosol, although several trace species (V, Cr, Mn, Ni, As, Cd, Pb) have been tentatively linked to negative health impacts e.g. Chen and Lippmann (2009). Daily-mean concentrations for these trace species determined from samples collected in Reykjavíð town over 4 consecutive days are shown in Fig. 6b. The species generally show little variation in concentration during the sampling period.

We assessed the environmental lability of the different species in the aerosol phase by a sequential leaching method. Fig. 6 shows the solubility of aerosol trace species. The figure also shows the enrichment factors (Mg-based EF, depicted by white circles on Fig. 6a) calculated based on the relative abundance of each element in the plume and in the magma, see e.g., Mather et al. (2012). Elements with $EF > 10$ are considered as volatile. The majority of the measured trace species were soluble in water or weak acid. The exception were the lanthanides, which were all poorly soluble, and also showed a generally low volatility. These results imply a high environmental mobility of trace metals deposited as aerosol from the Holuhraun plume, with near-immediate dissolution. Poorly soluble compounds, such as the lanthanides, also dissolve but over a longer timescale (Oelkers and Gislason, 2001).

4.2. Impact on air quality

Time series of major volcanogenic air pollutants, SO_2 gas, $PM_{2.5}$ and sulphate (SO_4^{2-}) aerosol were collected in two populated areas, Reykjavíð town and Reykjavík capital area. PM_{10} data are also available but we will focus our analysis on $PM_{2.5}$ which is the dominant size bin for volcanic aerosol as discussed in section 4.1. $PM_{2.5}$ is also a highly relevant factor impacting on human health, morbidity and mortality (Holgate, 2017).

4.2.1. Reykjavík capital area

During the course of the eruption, the European Commission (EC) air quality standards (EC Environment, 2016) for SO_2 exposure were exceeded 34 times for hourly limits ($350 \mu g/m^3$ hourly average) and 7 times for daily limits ($125 \mu g/m^3$ 24 h average), which also surpasses the number of permitted daily exceedances per year (max. 3 days). In the pre-eruption interval 2012–2014, SO_2 limits were never exceeded (Table 2).

Volcanogenic $PM_{2.5}$ mass concentrations in Reykjavík did not exceed the 24 hour-mean standard ($25 \mu g/m^3$) set by the World Health Organisation (WHO). The peak in $PM_{2.5}$ on 15 February 2015 (Fig. 7) is considered to be of a non-volcanic origin because

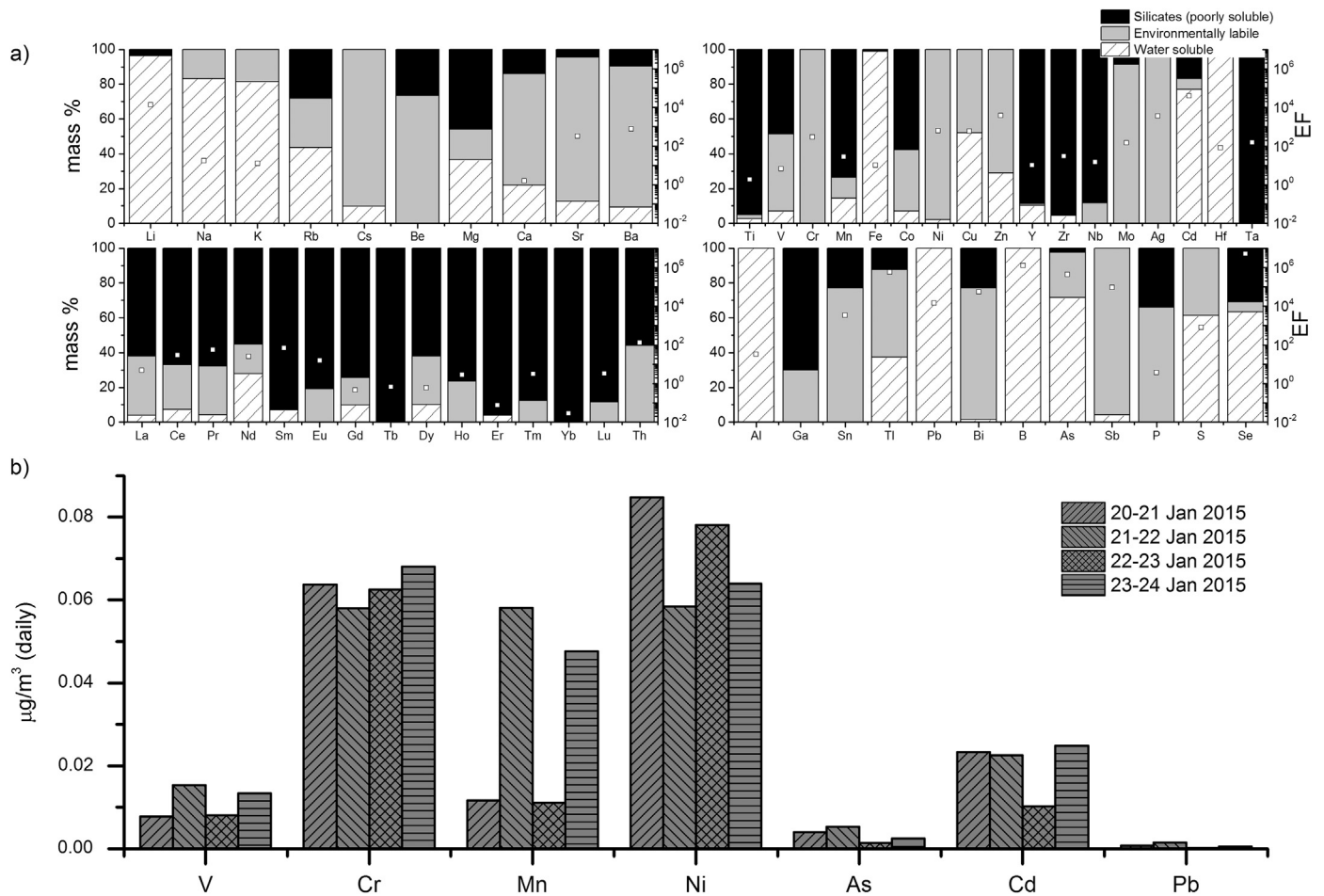


Fig. 6. **a)** Concentrations of all major and trace elements in the aerosol phase as measured in the populated area of Reykjavíð. The elements are shown in their solubility fractions*, normalised to 100%. Enrichment factor is also shown for elements where data exist. *Water soluble – milliQ extraction; Environmentally labile – weak acid extraction (HAHCl); Silicate – HF extraction. **b)** Concentrations of trace metal pollutants which have been linked to negative health impacts in four samples collected in Reykjavíð. The plot demonstrates that the difference in trace pollutant concentrations is relatively small between samples collected in a young plume (21–22 Jan. 2015) and mature plume (23–24 Jan. 2015).

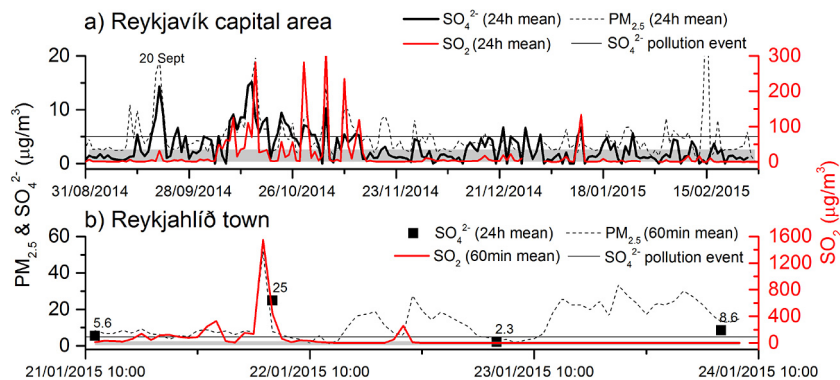


Fig. 7. Time series of SO_2 , $\text{PM}_{2.5}$ and sulphate (SO_4^{2-}) in **a)** Reykjavík capital area during the whole eruption (24-h mean) and **b)** Reykjavíð town 21–24 January 2015 (hourly-mean). Background sulphate concentration (mean + standard deviation) is shown by a grey bar (background data from Reykjavik used for both Reykjavík and Reykjavíð. Reykjavíð background is likely to be lower than Reykjavík due to its location).

it is not associated with an increase in sulphate and occurred after the eruption intensity had critically waned. The origin of this peak has not as yet been explained. It does not appear to be linked to a particular meteorological event (IMO, personal communication, February 2017). Potential explanations include nearby road or building works. The average hourly $\text{PM}_{2.5}$ concentration during the eruption ($4.8\text{--}4.9 \mu\text{g}/\text{m}^3$) was elevated above pre-eruption background levels by 20% (Table 3). This is low compared to the

percentage increase in SO_2 and sulphate aerosol (with increasing variation depending on wind direction, but approximately 2800% and 170%, respectively). However, if we consider only the days when the plume was present in Reykjavík ($n = 38$, see section 3.1 for definition) the average hourly value of $\text{PM}_{2.5}$ is $7.5 \mu\text{g}/\text{m}^3$, which is 47% higher than the pre-eruption background.

The maximum hourly $\text{PM}_{2.5}$ concentration during the eruption period ($91 \mu\text{g}/\text{m}^3$) was detected on one of the ‘plume-present’ days

(16 October 2014). But this $\text{PM}_{2.5}$ peak was lower than several peak concentrations during the non-eruptive period 2012–2014 (max $160 \mu\text{g}/\text{m}^3$ per hour, Table 2).

However, emissions from the eruption caused a significant change in the chemical composition of the aerosol, with a large increase in sulphate mass, both in hourly-mean ($\sim 170\%$) and peak concentrations ($\sim 300\%$), Table 2. Unlike SO_2 , air quality standards for sulphate are not available, and any definitions of sulphate ‘pollution events’ are somewhat arbitrary. In this discussion we set the limit at $5 \mu\text{g}/\text{m}^3$, based on the suggestion of Lioy and Waldman (1989) in a review of anthropogenic pollution in major cities 1930s–1980s. Longo et al. (2005) used the same reference for identifying volcanic pollution zones around Kilauea volcano in Hawaii. Compared to the background aerosol in Reykjavík, $5 \mu\text{g}/\text{m}^3$ is significantly higher than the background mean ($1.5 \mu\text{g}/\text{m}^3$, Table 2). During the 38 days when the plume was present in Reykjavík, SO_4^{2-} accounted for 90% of the $\text{PM}_{2.5}$ mass on average; and 30 out of the 38 days experienced SO_4^{2-} concentrations $\geq 5 \mu\text{g}/\text{m}^3$ (compared to a total of 8 days during the pre-eruption period 2012–2014). The maximum SO_4^{2-} daily average concentration ($15 \mu\text{g}/\text{m}^3$) was detected on 20 September 2014.

On multiple occasions throughout the eruption, $\text{PM}_{2.5}$ and sulphate mass concentration increased in Reykjavík without a corresponding increase in SO_2 mass concentration. For instance, there were at least 23 days when SO_4^{2-} exceeded $5 \mu\text{g}/\text{m}^3$ but SO_2 stayed within the EC standards ($< 125 \mu\text{g}/\text{m}^3$). One of the best examples is 20 September 2014 (Fig. 7a). Based on the results from dispersion modelling presented in Schmidt et al. (2015), we show here (Fig. 8) that these events were caused by an arrival in Reykjavík capital area of a plume with a low $S_{\text{gas}}/S_{\text{PM}}$, where sulphur has near-complete gas-to-aerosol conversion. A plume with a low $S_{\text{gas}}/S_{\text{PM}}$ ratio is considered mature with respect to sulphur chemistry. On occasions, the ‘same’ plume inundated the same area twice, first as a primitive high $S_{\text{gas}}/S_{\text{PM}}$ plume and then several days later as a mature, low $S_{\text{gas}}/S_{\text{PM}}$, plume.

Importantly, the mature, low $S_{\text{gas}}/S_{\text{PM}}$ plume was not forecast as part of volcanic pollution monitoring during Holuhraun. Daily forecasts of the plume dispersion issued by the IMO accounted only for SO_2 concentrations in a primitive high $S_{\text{gas}}/S_{\text{PM}}$ plume. For example, the forecast for 20 September 2014 predicted good air quality (‘no plume’) in Reykjavík (http://brunnur.vedur.is/kort/calpuff/2014/09/19/00/calpuff_island_so2.html) but our results show that $\text{PM}_{2.5}$ exceeded the recommended levels, and sulphate was $\gg 5 \mu\text{g}/\text{m}^3$ (Figs. 7a and 8b). Furthermore, results from dispersion modelling by (Schmidt et al., 2015) show an example of a ‘near-miss’ event (Fig. 8c), where a mature plume with concentrations of sulphate of $50\text{--}100 \mu\text{g}/\text{m}^3$, narrowly passed the densely populated south-east coast of Iceland. Based on these findings, we recommend that mature plumes are included in air pollution forecasting during future eruptions.

4.2.2. Reykjavík town

The peak SO_2 concentrations and the frequency of air quality exceedance (hourly and daily means) were higher in Reykjavík (88 hours/10 days) than Reykjavík (34 hours/7 days, Table 3), as Reykjavík was located much closer to the eruption site.

The $\text{PM}_{2.5}$ and sulphate time series are not as long-term in Reykjavík compared to Reykjavík. The data are nevertheless very important as they are a high resolution record of how the plume was fluctuating in intensity and composition at that location. The average and maximum hourly concentrations of both $\text{PM}_{2.5}$ and sulphate were 13 ± 9.5 and $11 \pm 10 \mu\text{g}/\text{m}^3$, respectively, which we consider to be significantly elevated above background ($4 \mu\text{g}/\text{m}^3$ and $1.5 \mu\text{g}/\text{m}^3$, respectively, in Reykjavík but likely to be lower in Reykjavík as discussed in section 2.5). Daily-mean sulphate con-

centrations exceeded $5 \mu\text{g}/\text{m}^3$ on 3 out of the 4 days of sampling (Fig. 7b).

In Reykjavík we made the same observation as in Reykjavík that the peaks in SO_2 and $\text{PM}_{2.5}$ were not always synchronous. The Reykjavík time line (Fig. 7b) shows two types of events: 1) SO_2 and $\text{PM}_{2.5}$ peak simultaneously at $\sim 5\text{AM}$ on 22 January 2015; and 2) $\text{PM}_{2.5}$ increases without a corresponding peak in SO_2 from $\sim 11\text{AM}$ on 23 January 2015. The source of the increase in $\text{PM}_{2.5}$ on 23 January is interpreted to be volcanic because sulphate is also elevated during the same time interval. This shows that there were episodes of a mature, low $S_{\text{gas}}/S_{\text{PM}}$ plume arriving in Reykjavík in the same way as was described in section 4.2.1 for Reykjavík capital area.

The concentrations of trace metals, including species that have been linked to negative health impacts, were similar when sampled in a primitive, high $S_{\text{gas}}/S_{\text{PM}}$ plume and a mature, low $S_{\text{gas}}/S_{\text{PM}}$ plume in Reykjavík (Fig. 6b). This suggests that mature Holuhraun plumes did not lose significant amounts of the metal-bearing aerosol, and were as potentially polluting as a more primitive plume with respect to these trace metals.

4.2.3. Implications for health impacts

Evidence suggests that the spread of tropospheric volcanogenic air pollutants during the Holuhraun eruption was reportedly the most extensive since the Laki eruption 1783–1784 CE. Holuhraun caused deterioration of air quality in populated areas $> 1000 \text{ km}$ from source in Europe (Gíslason et al., 2015; Schmidt et al., 2015; Twigg et al., 2016). For comparison of impact intensity, SO_2 concentrations during an intense degassing period in 2008–2009 of Kilauea volcano, Hawaii, never exceed the guidelines in the populated area of Kona in 80 km distance from the emission source. SO_2 guidelines have only been reported to have been exceeded within $\sim 30 \text{ km}$ radius (Hawaii State Department of Health, Clean Air Branch, 2010).

While most studies on the relationship between volcanogenic pollution and health agree that the impacts are generally negative (e.g., Baxter et al., 1982, 1990; Longo et al., 2008; Tam et al., 2016), there is no good consensus on the exact cause, or the mechanisms involved. The published air quality exposure limits for pure SO_2 are designed based on laboratory studies in volunteers with non-severe asthma (US EPA National Center for Environmental Assessment, R.T.P.N., 2008). This has shown that asthma sufferers are particularly sensitive to low levels of SO_2 , with symptoms including the rapid onset of constriction of the airways as is seen in asthma attacks. Air quality limits are set to protect this most vulnerable group. The evidence is weak on the long-term effects of repeated exposure to episodes of SO_2 pollution over time, such as occurs during prolonged eruptions. EC air quality standards are also not available for HCl or HF gas for periods over 8 h.

The health impacts of sulphate aerosol exposure in air pollution are much less understood. A major WHO review (WHO, 2013) concluded that there was no new toxicological evidence to support a causal role for inorganic sulphate in the health effects of $\text{PM}_{2.5}$, in accord with the comprehensive review on the subject by Schlesinger and Cassee (2003). However, epidemiological studies continue to report associations between sulphates and adverse impacts on human health. Postulated explanations include the possibility that sulphate is simply a marker for the causal agents in $\text{PM}_{2.5}$; or that toxic species may be formed in its chemical reactions with trace metals and the transition metals released in combustion processes. Sulphate has been reported to increase the solubility of iron in particles (Oakes et al., 2012), while metals may catalyse the production of sulphuric acid which in turn might react to produce toxicologically active soluble metal salts. The exact toxic mechanisms by which metals act are unknown, but free rad-

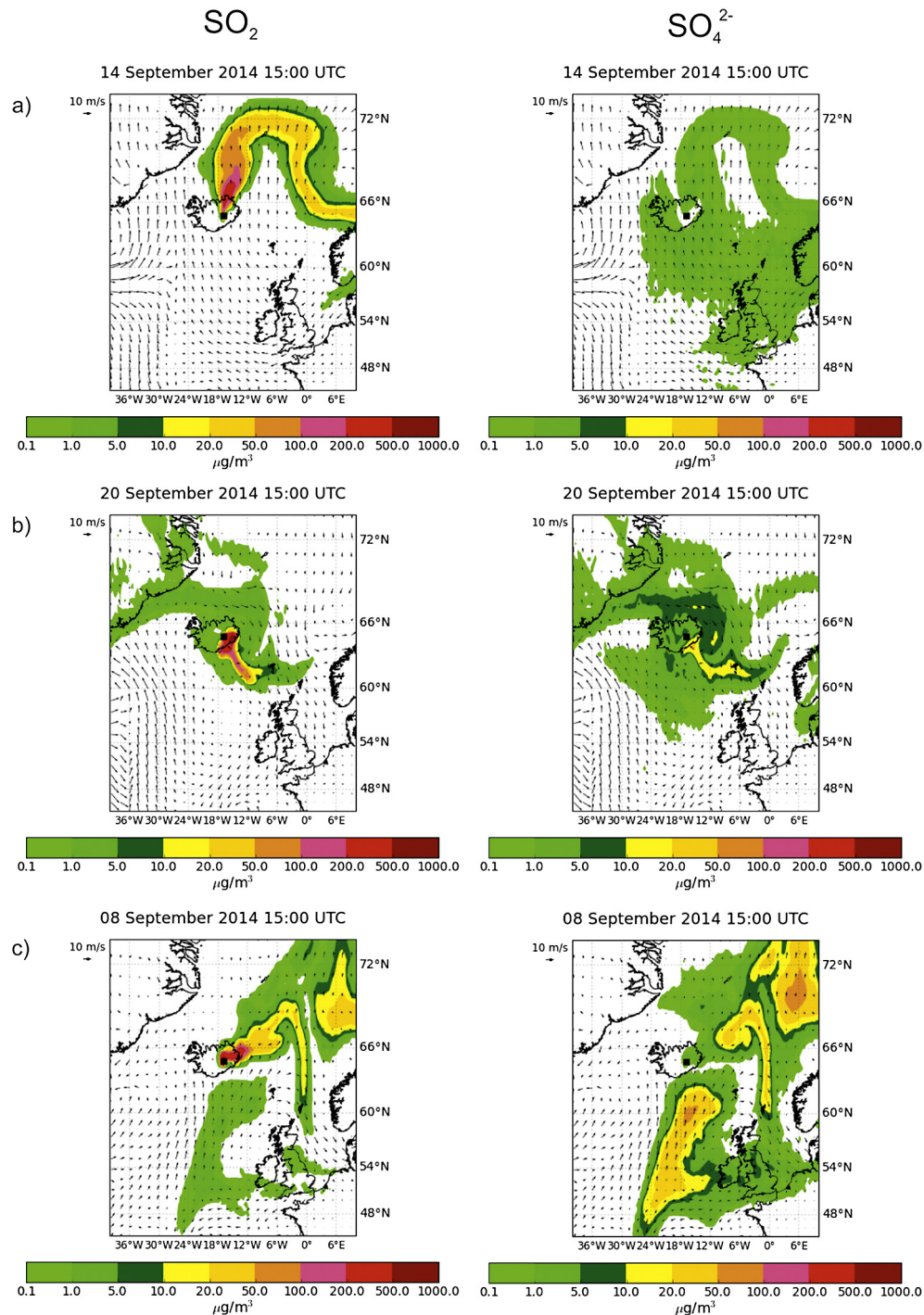


Fig. 8. Dispersion model of hourly-mean sulphur dioxide (SO_2 , left) and sulphate aerosol (SO_4^{2-} , right) surface mass concentrations ($\mu\text{g}/\text{m}^3$) for selected days in September 2014, based on Schmidt et al. (2015) (full animation 31 Aug. 2014–28 Sept. 2014 in supplementary material SM3). Panels (a) and (b) show a mature low $S_{\text{gas}}/S_{\text{PM}}$ plume reaching the Reykjavik capital area on 14 and 20 September 2014 (right), whereas SO_2 mass concentrations are very low in the same location on those days (left) Panel (c) shows a ‘near-miss’ situation with a highly sulphate-rich mature plume narrowly passing the densely populated southeast coast of Iceland on 8 September 2014.

ical generation has been proposed by many e.g., Kelly and Fussell (2015). Lippmann (2014) has also argued that sulphate represents the end stage of a chain of reactions in the aerosol that produces toxicologically active species, and that the hydrogen ion (acidity) is a key factor (he also stresses the potential importance of copper, nickel and vanadium, but the causal evidence for these and for other metals remains limited).

Volcanic plumes, as shown in this work and previous studies, are complex mixtures of gases and PM, some of which may be bio-reactive at low concentrations and add to the toxicity of the

plume. The health impact of these, when combined in the ambient air, might be greater than expected from their individual properties, but this has not been studied – the possibility of gases and fine particles synergistically enhancing the toxicity of SO_2 in volcanic plumes cannot be ruled out.

The dispersion of a primitive plume with high $S_{\text{gas}}/S_{\text{PM}}$ ratio was operationally forecast during Holuhraun eruption. Anecdotal evidence suggests that the public heeded the forecasts and limited the time spent outdoors when the plume was forecast to be present (EAI and Icelandic Directorate of Health, pers comm, Jan-

uary 2015). However, our results show, that on at least 18 days during the eruption the low $S_{\text{gas}}/S_{\text{PM}}$, mature plume was present in Reykjavík, while the forecast showed ‘no plume’. There is evidence to suggest that those days were noticed by local residents as having bad air quality. For example, on 20 September 2014 when sulphate concentrations in Reykjavík reached $15 \mu\text{g}/\text{m}^3$, but SO_2 was below exposure guidelines it was noted locally that: “*This day was very remarkable, eyes and throat were burning but SO_2 ...reached only $80 \mu\text{g}/\text{m}^3$. Later during the eruption when SO_2 exceeded $1000 \mu\text{g}/\text{m}^3$ [in the same location] eyes were not burning as much as on September 20*” (EAI, pers comm, August 2016).

Studies on the health impacts of the Holuhraun emissions should incorporate in their exposure assessments of at risk populations our findings on the variable concentrations of the SO_2 and sulphate aerosol, e.g., comparing the health impacts of plumes with a high $S_{\text{gas}}/S_{\text{PM}}$ ratio (‘primitive plume’) and the low $S_{\text{gas}}/S_{\text{PM}}$ ratio (‘mature plume’).

5. Conclusions

Holuhraun was the largest (1.6 km^3) and longest (6 months) volcanic eruption in Europe since the Laki eruption in late 18th century. The gas-and-aerosol rich plume of Holuhraun reached populated areas of Iceland up to at least 250 km distance. Our measurements showed that both the airborne plume, and the plume sampled at ground level contained enhanced concentrations of major (e.g. SO_2 , sulphate), and trace species (e.g. heavy metals), which on many occasions, were elevated above background levels by several orders of magnitude. The majority of these species were soluble in water or weak acid, implying high environmental mobility. We conclude that Holuhraun eruption caused a change in the average chemical composition of the atmospheric aerosol that was detectable at least as far as the downwind location of the Reykjavík capital area (250 km), in particular during the first two months of the eruption. The volcanic aerosol size was predominantly in the fine ($\text{PM}_{2.5}$) size fraction with a significant portion in the ultrafine fraction (PM_1).

There were two types of volcanic plume detected in the populated areas that impacted air quality in different ways. The first type, a ‘primitive’, plume had high concentrations of both SO_2 and sulphate, with a high $S_{\text{gas}}/S_{\text{PM}}$ ratio. The second type, a ‘mature’ plume had a low $S_{\text{gas}}/S_{\text{PM}}$ ratio, where sulphur had undergone significant gas-to-aerosol conversion. In the Reykjavík capital area (250 km downwind), there were at least 23 days when SO_2 exceeded $5 \mu\text{g}/\text{m}^3$, a concentration which previous studies have considered to constitute a pollution event (Lioy and Waldman, 1989; Longo et al., 2008) but SO_2 stayed within the EC air quality standards ($<125 \mu\text{g}/\text{m}^3$). This was caused by an arrival of a mature plume. Dispersion modelling of the volcanogenic pollutants shows that there were also near-miss events where a highly sulphate-rich mature plume narrowly passed the populated areas of Iceland without impacting upon air quality.

Both plume types had similar concentrations of trace metals (as measured in Reykjavík town 100 km downwind), including species that have been linked to negative health effects of air pollution from anthropogenic sources. The conclusion is that both primitive and mature plumes have the potential to be a source of environmental and air pollution, and in future major eruptions in Iceland both types warrant further investigation as undertaken in this study.

An innovation in Holuhraun eruption was real-time plume modelling in Iceland which enabled the path of the primitive plume to be forecast in advance, and warnings issued to the population. We recommend that in any future large fissure eruptions consideration be given to extending the forecasting of air pollution

events to include the low $S_{\text{gas}}/S_{\text{PM}}$, mature plumes, and careful assessment given to their possible wider dispersion.

As well as guiding in terms of future hazard and human health impact mitigation, this new understanding of the constituents of and chemical processing within the plumes from a large fissure eruptions has relevance in terms scaling up to Laki-scale events and the episodes of prolonged fissure activity (large igneous province volcanism) that punctuate the geological record.

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Appendix A. Supplementary material

Supplementary material related to this article can be found online at <http://dx.doi.org/10.1016/j.epsl.2017.05.025>.

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